Ordering of O vacancies in YBa$_2$Cu$_3$O$_{7-\delta}$

A. A. Aligia, A. G. Rojo, and B. R. Alascio

Centro Atómico Bariloche, 8400 Bariloche, Rio Negro, Argentina

(Received 19 February 1988)

Using a repulsive interaction of electrostatic origin between O ions lying at the plane which contains O vacancies, we determine the minimum energy structure for different values of the composition parameter δ. For $\delta = \frac{1}{2}$ or larger, the Cu-O chains disappear, and though the structure has no nearest-neighbor O ions, the main diffraction peaks show the same intensity as if the O ions were totally disordered. For small δ a long-distance ordering of the vacancies is obtained.

It is now well known that the high superconducting-transition-temperature T_c observed in YBa$_2$Cu$_3$O$_{7-\delta}$ compounds is very sensitive to the value of δ (oxygen content in the sample) and also to the heat treatment in O$_2$ atmosphere.[1−3]

Structural studies[4] show that the oxygen defects are located at the planes perpendicular to the tetragonal axis which bisect the shortest Ba-Ba distance along that axis. Moreover, near $\delta = 0$, the O ions rearrange themselves, forming Cu-O chains [see Fig. 1(a)]. As a consequence of the ionic core repulsion, the a_2 lattice parameter is $\sim 1.6\%$ larger than the a_1 parameter and the structure is orthorhombic. For temperatures above $T_0 \sim 700\,°C$, a_1 and a_2 become equal. The diffraction peaks were interpreted in that case as corresponding to a disordered O structure in the above-mentioned planes [see Fig. 1(b)].

In fact, since the number of carriers is low in these compounds, the Coulomb interaction between O ions is poorly screened at distances of the order of their nearest-neighbor distance ($3.9/\sqrt{2}$ Å). Then, the electrostatic en-

ergy per unit cell should be a fraction of a Rydberg larger for the structure of Fig. 1(b). The entropy part of the free energy at a temperature of the order of T_0 is much smaller than this energy difference, and we expect that the difference in electronic energy (which depends on the band filling) is also smaller. We thus conclude that the totally disordered structure does not occur and that the system avoids placing two O ions at their nearest-neighbor distance for any $\delta > 0$.

Similar conclusions were obtained in experimental[5] and theoretical[6] studies of the change in the lattice parameters with oxygen content. These studies also ascribe the origin of these changes to the ion-ion Coulomb forces. An important feature of the orthorhombic to tetragonal transition is the decreasing of oxygen content with temperature, the transition taking place seemingly at $\delta = 0.5$.[4,7] For $\delta \geq 0.5$, it is then possible that the ground state of the system is an ordered structure whose diffraction pattern bears resemblance with that of the disordered structure. Our calculations of the energies involved confirm this conclusion.

We consider a repulsive interaction $V(R) = A/R \times \exp(-R/\lambda)$ where R is the distance between O ions, and λ a screening parameter. According to experiments which determine the order of O vacancies for small δ,[8,9] the interaction is still important at distance $R \sim 11$ Å. If we take $\lambda \sim 3$ Å, we obtain $V \sim 0.1$ eV for $R \sim 11$ Å and $A = 4e^2$.

The Hamiltonian of the system can be written in the form

$$H = \epsilon_0 \sum_i n_i + \frac{1}{2} \sum_{i,j} V_{ij} n_i n_j , \qquad (1)$$

where $n_i = 1, 0$ is the number of oxygen ions at site i and the sum runs over all possible positions of the oxygen ions in the plane of interest. [See Fig. 1(b).] The allowed positions span a simple square lattice [we neglect the effect of the possible orthorhombic distortion on the parameters of (1)]. The first term of Eq. (1) represents the binding energy of a single O ion. The second term represents the interaction energy between oxygen ions. We have taken

$$V_{ij} = \frac{A}{|\mathbf{R}_i - \mathbf{R}_j|} e^{-|\mathbf{R}_i - \mathbf{R}_j|/\lambda} , \qquad (2)$$

where A is a constant of the order $4e^2$. If the oxygen defects alter the ionic charges, then A will be δ dependent,
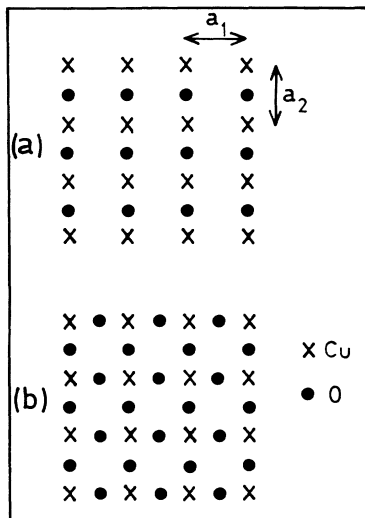

FIG. 1. Structure of the planes which contain the oxygen defects according to Ref. 4. (a) Orthohombic structure: the O positions aligned with the Cu ions along one of the main axes are occupied preferentially. (b) Tetragonal structure: all positions are occupied with the same probability.

but its value does not affect the minimum-energy structure for a given δ.

Hamiltonian (1) is isomorphic to an Ising model in the presence of a magnetic field with long-range antiferromagnetic interactions. We have calculated the minimum energy structure for different occupation probabilities of the O sites in the relevant plane. This probability p is related to the structural parameter δ by

$$p = \tfrac{1}{2}(1 - \delta). \tag{3}$$

Guided by our numerical calculations in the range $\tfrac{1}{2} \leq p \leq \tfrac{1}{5}$, we have assumed that for $p = 1/n$, where n is an integer, the minimum energy configuration is given by a simple Bravais sublattice of the square lattice spanned by sites between any two Cu ions. The area of the sublattice unit cell is n times that of the square lattice. The task is reduced in this way to comparing the energies of all nonequivalent sublattices of the square lattice with a given unit cell area.

Since Hamiltonian (1) maps into itself when written in terms of the number of vacancies at each site, the results can be extended straightforwardly to concentrations of the form $p = 1 - 1/n$.

Taking advantage of the fact that for $p = \tfrac{1}{2}$ the minimum energy structure coincides with that of Fig. 1(a) (O ions and O vacancies occupying two equal interpenetrating sublattices), we can extend the method to concentrations $p = (1 - 1/n)/2$ with the assumption that the sublattice of O vacancies remains empty when new vacancies are added. The assumption is valid for $p \lesssim \tfrac{1}{2}$. For smaller concentrations the O ions reorder, occupying both sublattices.

We have investigated in detail the concentrations $p = 1/n$ and $p = (1 - 1/n)/2$ with n integer. In Table I, we list the basis vectors of the resulting minimum-energy simple Bravais lattices, for n up to 10.

We find that among all the possible simple Bravais lattices for n fixed, the lowest-energy configuration is the one
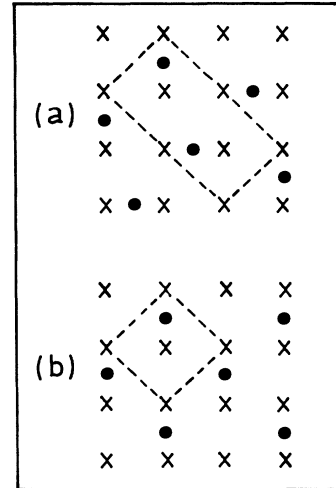

FIG. 2. Structures for $p = \tfrac{1}{4}$: (a) ground state; (b) first excited state with the O ions in a simple Bravais lattice. The dashed lines indicate a possible choice of unit cell.

the most similar to an hexagonal structure with the same number of atoms per unit surface. This is the minimum energy structure for O positions not constrained to be in a square lattice.

As an illustration, the ground-state structures for $p = \tfrac{1}{4}$ and $p = \tfrac{1}{3}$ are given in Figs. 2(a) and 3(a), respectively. The one corresponding to $p = \tfrac{1}{2}$ coincides with the experimentally observed [see Fig. 1(a)]. Instead, the $p = \tfrac{1}{4}$ structure differs from the totally disordered one proposed to account for the neutron-diffraction results [see Fig. 1(b)]. In fact, as can be seen from Eq. (4) below, the structural determination of both structures show the same intensity for the reciprocal-lattice vectors of the disordered one [neglecting a distortion much smaller than 1.6%
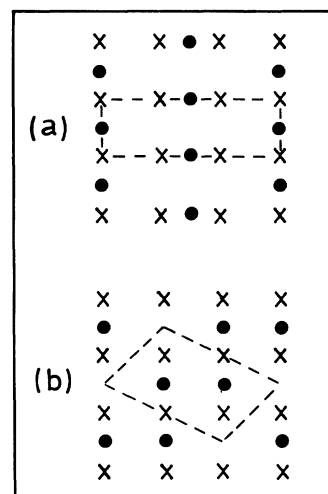
TABLE I. Basis vectors of the Bravais lattices which describe the structure of minimum energy for the following probability of occupation of the oxygen sites. (i) $p = 1/n$. The Bravais lattices describe the positions of the oxygen ions. (l,m) means $l(\mathbf{a}_1 + \mathbf{a}_2)/2 + m(\mathbf{a}_1 - \mathbf{a}_2)/2$. (ii) $p = \tfrac{1}{2} - 1/2n$. The Bravais lattices indicate the position of the additional vacancies added to the structure with $p = \tfrac{1}{2}$ [Fig. 1(a)]. Here, $(l,m) = l\mathbf{a}_1 + m\mathbf{a}_2$. (The approximation that the sublattice of vacancies for $p = \tfrac{1}{2}$ remains empty for $p = \tfrac{1}{2} - 1/2n$ breaks down for small $n \sim 3$.)

n	$\mathbf{V}_1$	$\mathbf{V}_2$
2	(1,1)	(−1,1)
3	(−1,1)	(1,2)
4	(1,2)	(2,0)
5	(1,2)	(2,−1)
6	(−2,2)	(2,1)
7	(−3,1)	(1,2)
8	(−2,2)	(1,3)
9	(0,3)	(3,1)
10	(−3,1)	(1,3)

FIG. 3. Structures for $p = \tfrac{1}{3}$: (a) ground state; (b) excited state of lowest energy among the ones obtained adding vacancies to the $p = \tfrac{1}{2}$ structure of Fig. 1(a).

in the $\mathbf{a}_1 + \mathbf{a}_2$ direction, which probably occurs in the structure of Fig. 2(a)]. If the structures which we find for $p \neq \frac{1}{2}$ were periodic in the direction normal to the planes of interest, new and weaker Bragg peaks would appear as a consequence of the larger unit cell.

The intensities of the scattering peaks for the reciprocal-lattice vectors $\mathbf{G}$ of the smallest unit cell (orthorhombic or tetragonal, see Fig. 1) can be classified according to the components of $\mathbf{G}$ parallel to the plane of interest. For any structure, the intensity is proportional to

$$I = |f_{Cu}(\mathbf{G}) + [(-1)^{m_1}p_1 + (-1)^{m_2}p_2]f_0(\mathbf{G})$$

$$+ \sum_L' e^{-i\mathbf{G}\cdot\mathbf{R}_L}f_L(\mathbf{G})|^2 , \tag{4}$$

$$\mathbf{G}_{\parallel} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 .$$

Here $\mathbf{b}_i = 2\pi\mathbf{a}_i/|\mathbf{a}_i|^2$, $f_E(\mathbf{G})$ is the form factor of the E ion times the exponential of the Debye-Waller factor, p_i is the probability of finding an oxygen ion in the plane of interest aligned with the Cu ions in the direction of $\mathbf{a}_i$. $\sum_L'$ refers to all the atoms in the unit cell which are not contained in the plane, and m_1 and m_2 are integers.

If the translational symmetry along the $\mathbf{a}_1 \times \mathbf{a}_2$ direction were preserved, the structure of Fig. 2(a) would manifest itself at the following wave vectors and intensities [with the same proportionality factor as in Eq. (4)]

$$\mathbf{G}_{\parallel} = m_1(\mathbf{b}_2 - \mathbf{b}_1) + m_2(\mathbf{b}_2 + \mathbf{b}_1)/4 ,$$

$$I = \frac{1}{4}|f_0(G)|^2 . \tag{5}$$

Here, m_2 is any integer except a multiple of 4. At temperature larger than the orthorhombic-to-tetragonal transition, these peaks might not be seen for two reasons: (1) The interaction energy between different planes is small, and (2) depending on the value of λ, the above-mentioned temperature is a few times smaller or of the order of the energy difference between the two structures shown in Fig. 2 (see Fig. 4). Our analysis at finite temperatures using Monte Carlo methods[10] shows that the structure of Fig. 2(a) with increasing temperature evolves to an ensemble of small clusters of both structures located and oriented at random. This kind of mixture still has $p_1 = p_2 = \frac{1}{4}$ displaying the same peaks as the totally disordered structure or the structure of Fig. 2(a) for the wave vectors of Eq. (4), but the intensities for the $\mathbf{G}_{\parallel}$ of Eq. (5) are still much smaller making a differentiation from the totally disordered structure difficult. In any case, to the best of our knowledge, these peaks have not been investigated experimentally.[4]

Instead, the perfect structure of Fig. 2(b) would display a scattering pattern similar to the one corresponding to the orthorhombic structure.

In both structures of Fig. 2 and in the ground structures for $p < \frac{1}{4}$, all the copper atoms in the plane have coordination 3 (counting two oxygen atoms which are out of the plane). This type of T-shape coordination for copper has not been observed in other substances and might be energetically unfavorable,[5,6] but reducing the number of threefold-coordinated copper atoms for dilute concentrations would imply a considerable increase in the dominant
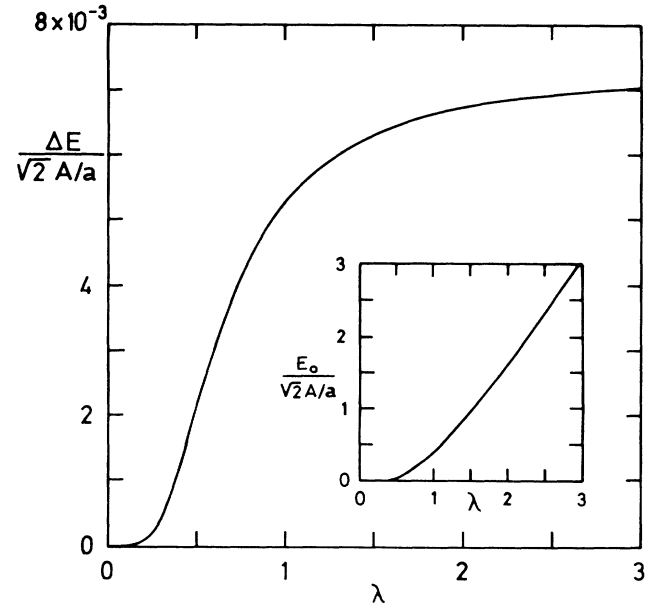

FIG. 4. Energy of the structure shown in Fig. 2(b) with respect to the ground state of Fig. 2(a) as a function of the screening length λ [see Eqs. (1) and (2)]. The inset corresponds to the ground-state energy.

O-O repulsion. Since, in the dilute structures of lower energy, the immediate surrounding of each atom is the same, the electronic energy neglected in our model does not change our conclusions concerning the ground-state configuration for a given p.

For $p = \frac{1}{3}$, the ground-state structure [Fig. 3(a)] has $p_1 = p_2$, like the totally disordered tetragonal structure. Nevertheless, we expect a distortion $a_2 > a_1$ as it happens in the orthorhombic phase. This difference would manifest in the existence of twin planes[8] and in the size of the reciprocal-lattice vectors. Contrary to our results, structural studies[4,11] suggest that $p_1 \neq p_2$ for $p > \frac{1}{4}$. We believe that this discrepancy could be due to two effects which we have neglected: (i) the elastic energy involved in the orthorhombic distortion that makes the two sites inequivalent and splits the energy ϵ_0 of Eq. (1), and (ii) an energy of chemical or electronic origin that destabilizes the threefold-coordinated Cu atoms. Both effects decrease in importance with increasing $|p - \frac{1}{2}|$. In Fig. 3(b) we show a structure with $p_1 = 0$ and $p_2 = \frac{2}{3}$, obtained adding vacancies to the $p = \frac{1}{2}$ structure. While in the structure of Fig. 3(a), $\frac{2}{3}$ of the Cu atoms have T-shape coordination, this number is reduced to $\frac{1}{2}$ for the structure of Fig. 3(b). This fact and elastic energies could reduce the difference in energy between structures and make a coexistence at moderate temperatures possible.

We have performed numerical simulations for different occupation probabilities starting from a random configuration of O ions in lattices of size $\sim 15 \times 15$ with periodic boundary conditions, and then looking for a local minimum of energy interchanging O ions and vacancies. The results support our assumption that for $p = 1/n$ the oxygen ions arrange in a simple Bravais lattice. For inter-

mediate concentrations (neglecting some random local structures which always appear in the numerical calculations), we observe a segregation in small clusters of the two neighboring structures of the form $1/n$ (see Fig. 5). These results were confirmed by Monte Carlo calculations in which the system was "annealed" from a high-temperature equilibrium configuration.[10] We conjecture that this two-phase state could be connected with the plateau observed in the variation of T_c with composition.[2,3]

As we mentioned before, the results for $p = 1/n$ can be translated to $p = \frac{1}{2} - 1/2n$ for sufficiently large n. (For small n, a reordering of the O ions lowering the energy becomes possible. The case $n = 3$ is illustrated in Fig. 3.) For $\delta = 0.125$, the ground-state structure is given in Table I in the entry $n = 8$. The first excited structure with a small excitation energy has unit vectors $(2,2)$ and $(2, -2)$, corresponding to a $2\sqrt{2} \times 2\sqrt{2}$ structure. Both structures are contained in the unit cell of parameters $4\sqrt{2}a_1 \times 2\sqrt{2}a_1$, in agreement with the experimental observations.[9]

We mention that an accurate analysis of the chemical potential for different O partial pressures and temperatures is rather difficult because one expects the energy ϵ to remove an oxygen atom from the gas and place it in the lattice to depend on δ and to grow with temperature. The variation of the constant A and the screening parameter λ with δ must also be taken into account, due to the increase in the number of carriers with O concentration.

In summary, based on the interatomic electrostatic interactions, we have studied the ordering of O ions and vacancies in $YBa_2Cu_3O_{6+2p}$, where p is the probability of occupancy of the sites lying between two copper ions in the planes perpendicular to the c axis which bisect the Ba-Ba segment.

We obtain that for $p = 1/n$ where n is an integer, the oxygen ions arrange themselves in a simple Bravais lattice which represents the smallest possible distortion of the hexagonal lattice, to minimize the energy. For intermediate values of p (and probably for values of p for which the possible Bravais lattices deviate too much from the hexagonal structure), the system segregates into small clusters of two phases of neighboring p. Due to the symmetry of the model, the results for probability p can be extended to $1 - p$ interchanging O ions and vacancies. Using this fact and the topology of the ground state for $p = \frac{1}{2}$ (neglecting the orthorhombic distortion), the results for $p = 1/n$ can be translated to $p = \frac{1}{2} - 1/2n$ for large n, i.e., the additional O vacancies added to the perfect orthorhombic structure of Fig. 1(a) arrange themselves in a simple Bravais lattice at small temperatures. The results which we obtain for the ordering of these vacancies agree with re-
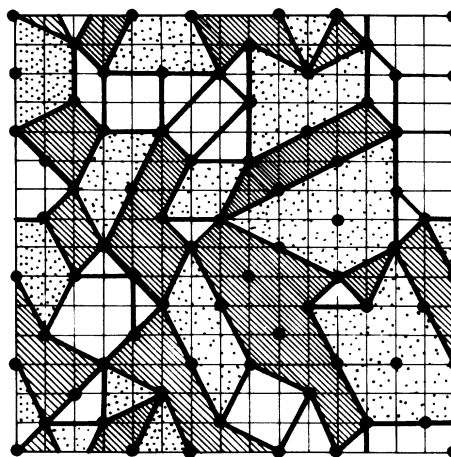

FIG. 5. O ion positions that result from a typical run of our numerical program, which finds a local minimum for $p = \frac{7}{24}$ in a square lattice of possible oxygen positions of size 15×15 with periodic bondary conditions and $\lambda = a/\sqrt{2}$. The dotted and hatched areas are clusters with the ground-state structures for $p = \frac{1}{4}$ [Fig. 2(a)] and $p = \frac{1}{3}$ [Fig. 3(a)], respectively. Smaller clusters with the ground structure for $p = \frac{1}{2}$ and $p = \frac{1}{5}$, the first two excited structures for $p = \frac{1}{4}$ and empty spaces can also be seen. The Cu sites are not shown.

cent electron-diffraction studies.[9] It is interesting to note that for large n, if the interactions between O ions beyond the fourth-nearest-neighbor interaction can be neglected, it is more convenient to arrange the additional vacancies in twin boundaries, separating regions of $p = \frac{1}{2}$ with a different orientation of the Cu-O chains.

Also, the ground structure for $p = \frac{1}{4}$ is compatible with the structural determinations (which investigated distances up to 3.95 Å and proposed a totally disordered structure).[4] The discrepancies with the experimental results[4,11] for $p \sim \frac{1}{3}$ are probably due to our neglect of elastic energies and the destabilization energy of T-shape coordinated Cu ions. While there is agreement with experiment on the fact that the Cu-O chains disappear at $\delta = 0.5$ ($p = \frac{1}{4}$) with increasing δ, the experimental results were interpreted in terms of an order-disorder transition[4] and our results suggest that the transition takes place between different ordered phases.

[1]K. Kadowaki, Y. K. Huang, M. Van Sprang, and A. A. Menovsky, Physica B **145**, 1 (1987).

[2]P. Monad, M. Ribault, F. D'Yvoire, J. Jegoudez, G. Collin, and A. Revcolevschi, J. Phys. (Paris) **48**, 1369 (1987).

[3]M. Tokumoto, H. Ihara, T. Matsubara, M. Hirabayashi, N. Terada, H. Oyanagi, K. Murata, and Y. Kimura, Jpn. J. Appl. Phys. (to be published).

[4]J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987), and references therein.

[5]A. Renault, J. K. Burdett, and J. P. Pouget, J. Solid State Chem. **71**, 587 (1987).

[6]M. H. Whangbo, M. Evain, M. A. Beno, V. Geiser, and J. M.

Williams, Inorgan. Chem. (to be published).

[7]I. K. Schuller (unpublished).

[8]G. Van Tendeloo, H. W. Zandbergen, and S. Amelinckx, Solid State Commun. 63, 389 (1987).

[9]M. A. Alario-Franco, C. Chaillout, J. J. Capponi, and J. Chenavas, Mater. Res. Bull. 22, 1685 (1987).

[10]A. A. Aligia, A. G. Rojo, and B. R. Alascio, in *Progress in High Temperature Superconductivity* (World Scientific, Singapore, in press).

[11]C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chenavas, P. Strobel, and M. Marezio, Solid State Commun. 65, 283 (1988).